Studies on Multiphase Heck Coupling Reactions with Palladium Catalysrts(パラジウム触媒を用いた多相系Heckカップリング反応に関する研究)

	ちょう　ふんぎょく
氏　　名	趙　　鳳　玉
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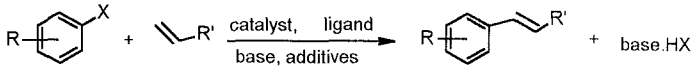
指　導　教　官	東北大学教授　宮下 徳治
論文審査委員	主査　東北大学教授　宮下 徳治　東北大学教授　井上 祥雄
	東北大学教授　飯野 雅

論　文　内　容　要　旨

1. Introduction

Heck reaction has received considerable attentions in recent years as it offers versatile method for generating new carbon-carbon bond (Scheme 1). The reaction is normally carried out using a palladium catalyst, phosphine ligand and a base in homogeneous mode of operation. However, the reaction suffers from severe limitations that have so far precluded widely spread industrial applications. Relatively large amounts of catalysts are needed for reasonable conversions and catalyst recycling is often hampered by early precipitation of palladium black. A few approaches have been described in improving homogeneous catalyst systems with sterically hindered phosphine ligands, a large excess of coordinating ligands, and high pressure conditions.



Scheme 1　Heck reaction

In view of practical and industrial applications, the use of heterogeneous catalysts may be promising. Therefore the aim of the present work is to develop an effective heterogeneous catalytic process for Heck reaction and the main works have been undertaken to study the Heck reactions with conventional supported palladium catalysts and biphasic and SLPC catalyses using organopalladium complexes. Besides these, basic studies on homogeneous Heck reaction have also been made.

2. Experimental

A commercial 10% palladium on activated carbon sample was purchased from Wako Pure Chemicals Industries. Other 1% palladium catalysts were prepared by ion exchange with $Pd(NH_3)_4Cl_2$ as precursor using SiO_2, C and smectite supports. The Pd/C samples were reduced by flowing hydrogen at 200℃ for 3 h and the others at 450℃ for 3 h before reaction. The surface areas of supports were determined by nitrogen adsorption method (BET). The areas of exposed palladium atoms were measured by hydrogen adsorption at room

temperature. The Heck reactions were carried out in a 50-ml round bottom flask at temperatures of 50~85℃ or a 100-ml autoclave at temperatures of 90~160℃. The reaction mixture were sampled and analyzed by GC and the conversion was determined from the amount of iodobenzene consumed. The amount of palladium leaching out into the solution was measured using atomic absorption spectroscopy.

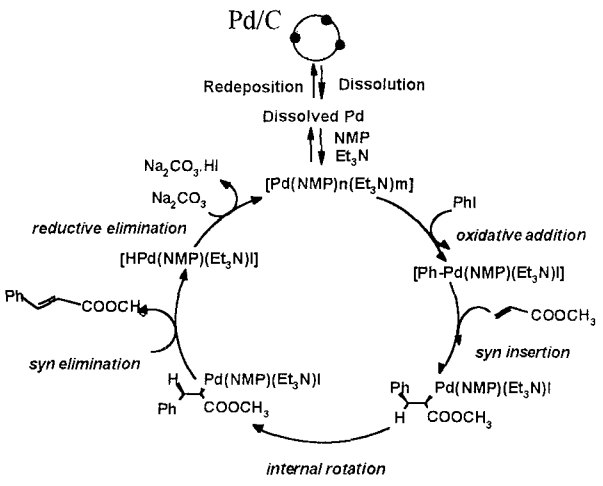
3. Results and discussions

- Homogeneous Heck Reaction with $Pd(OAc)_2/PPh_3$ Catalysts

The basic studies on homogeneous Heck reaction have been made. Effects of various reaction parameters such as the concentrations of iodobenzene, methyl acrylate, triethylamine, ligand (PPh_3), and catalyst have been studied, and the kinetics of the Heck reaction has also been analyzed. There is not a rate-determining step in the reaction of iodobenzene with methyl acrylate catalyzed by $Pd(OAc)_2/PPh_3$ catalyst. PPh_3/Pd ratio has a significant effect on the rate of reaction. In nonpolar solvents, the rate of reaction passes through a maximum at $PPh_3/Pd=2$, and the precipitation of free palladium particles was observed at $PPh_3/Pd=0$. However, in the polar solvent of NMP, the rate of reaction is rather high at $PPh_3/Pd=0$, as NMP acts as a ligand to form an active complex with palladium, which is rather stable and more active catalyst compared with conventional palladium complex $Pd(PPh_3)_2$.

- Heterogeneous Heck Reaction with Conventional Supported Palladium Catalysts

The Heck reactions proceed homogeneously in the reaction solution even though the heterogeneous catalysts are used. The solvent NMP and organic base Et_3N coordinate with palladium to form an active catalytic complex, making palladium species to leach out into reaction solution, and thus the reaction is mainly catalyzed with these dissolved palladium species in the solution. Therefore, high activity is obtained with a TOF of 70000 h^{-1} for the reactions of iodobenzene and methyl acrylate. It is about 10000 times larger than the results reported in the literature. The leaching of palladium is easier for the reduced catalyst compared with the untreated and calcined catalysts. In addition, active species of palladium (0) complex is more easily formed in the solution with the reduced catalyst, so the rate of reaction is larger in the reactions with reduced catalysts. The dissolved palladium can re-deposit to the surface of support after the reaction is completed (at the 100% conversion of iodobenzene). The presence of mixed bases accelerates the rate of reaction largely and promotes the palladium re-deposition, and temperature and the chemical properties of support also affect the palladium re-deposition. The dissolved palladium can re-deposit onto the carbon support completely at a high temperature of 160℃, and the recovered supported palladium catalysts can be reused for several times without loss in activity and selectivity. The mechanism of the Heck reaction with supported palladium catalyst is shown in Scheme 2.



Scheme 2 Mechanism of Heck reaction

The addition of water into the solvent NMP precipitates colloidal palladium particles, while it promotes the rate of reaction due to the hydrogen bond forming between water and NMP, which affects the activity of palladium species.

The vinylations of bromobenzene and chlorobenzene also proceed homogeneously with dissolved palladium species. By-products of benzene and biphenyl are also formed in the reactions of chlorobenzene and bromobenzene. The nature of the halogen in the organic substrate not only affects oxidative addition but also affects the following stages of the catalytic cycle.

- Transfer of Palladium between Support and Solution

The transfer of palladium depends on the surface nature of supports and the reaction conditions. Under the reaction conditions used, palladium can transfer from one support to another support, from homogeneous solution to the additional support and free palladium particles. The homogeneous palladium species can be collected by adding additional support to the reaction solution and it can be recovered through re-dissolving in the reaction solution. The recovered homogeneous catalysts exhibit the same activity as does the fresh one. Therefore a recyclable homogeneous catalytic process is developed for the Heck reaction.

- Heck Reaction with Biphasic and Supported Liquid Phase Catalysts

In the biphasic system, the reaction occurs at the interface between the organic and catalyst phases. The activity of several metals used is in the order of Pd >Ni >Ru >Co >Pt. After the reaction is completed, the catalyst phase is easily separated from the Heck product contained in organic phase, and its recycling can be carried out under the same reaction conditions. The palladium complex of $Pd(TPPTS)_4$ shows that it can be reused for several times without loss in activity and selectivity. In addition, the by-product, base adduct, is easily separated from the Heck product and it can be recycled with catalyst phase having no effect on the reaction rate and selectivity during the subsequent reactions.

In the SLPC system, both Ni and Pd were examined for the Heck reactions. Ethylene glycol is an effective solvent for preparing SLPC since it exhibits higher activity and stability at higher temperature compared with water. The rate of reaction increases with the amount of support added mainly due to the increase in catalyst surface area, and thus the interface between catalyst phase and organic reactant phase is enlarged. The catalyst can be recovered with a simple procedure and reused for several times without loss in activity and selectivity.

4. Conclusions

An effective Heck reaction process has been developed with supported palladium catalysts. A more active catalytic species has been found, which is a palladium complex formed from the coordination of solvent NMP and base Et_3N with palladium and which makes palladium leach out into reaction solution. This system shows a special merit that the leached palladium can re-deposit to the support after they finished their task for catalyzing the reaction, and thus the catalyst can be recycled and reused. Another merit of this system is that the catalyst shows a very high activity with a TOF of 70000 h^{-1}, which is comparable with homogeneous activity. Homogeneous catalyst can be collected and recycled through adding the palladium free supports into the reaction solution. Both bi-phasic and SLPC are effective heterogenized reaction systems for Heck reactions.

審査結果の要旨

有機合成用触媒として高活性な均一系有機金属錯体触媒が開発されつつあるが，触媒と生成物の分離及び触媒のリサイクルが困難であるなどの欠点があり，工業的応用の大きな問題となっている。著者は，この問題を解決するためには反応系を不均一化することが肝要と考え，工業的に重要な Heck カップリングを対象反応として，いくつかの不均一系パラジウム触媒系の有効性を検討し，リサイクル可能な触媒反応系の開発に成功した。本論文は，この研究成果をまとめたもので，全文7章よりなる。

第1章は序論であり，本研究の背景及び目的を述べている。

第 2 章では，本研究で用いた触媒の調製と特性評価，反応実験の方法と解析について記述している。

第 3 章では，不均一系反応を考察する基礎としてパラジウム錯体触媒を用いた均一系反応の動力学的特徴を検討した結果を述べている。ある種の極性溶媒はそれ自身が配位子として作用するという重要な知見を得ている。

第 4 章では，担持パラジウム触媒を用いた固－液反応の結果を示し，反応の特徴と反応機構を検討している。溶媒に溶出したパラジウムが活性種となって反応は均一溶液中で進行し，反応後には溶出したパラジウムが再び担体に析出し回収・リサイクルできることを見出した。これは，通常の担持触媒の有効性を示す有用な成果である。

第 5 章では，均一系および不均一系触媒 を用いて，パラジウム種の物質移動過程を調べた結果を述べている。担体の表面性状や反応条件によって，パラジウム種は担体表面，溶媒，コロイド粒子間を可逆的に移動することを明らかにした。これは，リサイクル可能な反応システムを設計する上で非常に重要な成果である。

第 6 章では，有機金属錯体を触媒とした液－液2相系と担持液膜触媒を用いた反応結果を述べている。両不均一系の活性，選択性，安定性，再利用性を検討し，有効性を明らかにしている。

第7章で結論である。

以上要するに本論文は，各種の不均一系 Heck 反応を研究して，リサイクル可能な触媒反応系の構築に成功するとともに，リサイクル性に関係する活性種の不均一化と物質移動過程の基礎を詳しく解析して明らかにしており，材料化学と触媒工学の発展に寄与するところが少なくない。

よって，本論文は博士（工学）の学位論文として合格と認める。